

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 972 862 A2

(12)

## EUROPEAN PATENT APPLICATION

(43) Date of publication:

19.01.2000 Bulletin 2000/03

(51) Int. Cl.<sup>7</sup>: C25D 11/36, C25F 1/00

(21) Application number: 99112414.0

(22) Date of filing: 29.06.1999

(84) Designated Contracting States:

AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE

Designated Extension States:

AL LT LV MK RO SI

(30) Priority: 01.07.1998 JP 18583098

(71) Applicants:

- NIHON PARKERIZING CO., LTD.  
Chuo-ku, Tokyo (JP)
- Fujisyouji K.K.  
Hashimashi, Gifu 501-6257 (JP)

(72) Inventors:

- Kobayashi, Naoyuki,  
c/o Nihon Parkerizing Co., Ltd  
Tokyo (JP)

- Moriyama, Atsushi,  
c/o Nihon Parkerizing Co., Ltd  
Tokyo (JP)
- Takagi, Shigemasa,  
c/o Fujisyouji K.K.  
Gifu 501-6257 (JP)
- Katsumata, Tomoaki,  
c/o Fujisyouji K.K.  
Gifu 501-6257 (JP)

(74) Representative:

Sajda, Wolf E., Dipl.-Phys. et al  
MEISSNER, BOLTE & PARTNER  
Widenmayerstrasse 48  
80538 München (DE)

## (54) Method for forming a phosphate film on steel wires and apparatus used therefor

(57) A method and an apparatus are disclosed which are suitable for promptly forming a phosphate film of excellent performance for cold drawing on steel wires (1). The steel wires (1) are descaled by a cathodic electrolysis in an acid solution, and thereafter, a phosphate film is formed by a cathodic electrolysis on the steel wires. Contacting with a solution containing colloidal titanium is preferably carried out between a cathodic descaling process (2) and a phosphate film forming

process (3). Descaling in a cathodic electrolysis may be performed in an acid solution at a temperature of lower than 90 °C and with a current density of 1 to 100 A/dm<sup>2</sup>. Phosphate film forming (3) may be performed by using an electrolyte containing Zn ions, phosphoric acid ions and nitric acid ions, at a temperature of lower than 90 °C with a current density of 1 to 100 A/dm<sup>2</sup> and for a period of 1 to 30 seconds.

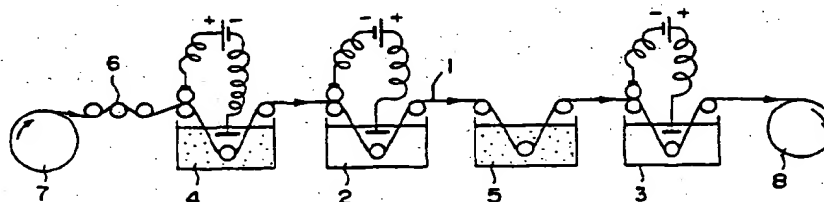


Fig. 1

EP 0 972 862 A2

## Description

Field of the Invention

5 [0001] Hot rolled or heat treated steel rods and steel wires, in the following abbreviated as steel wires, are often provided for a cold drawing process. Before carrying out the cold drawing process, usually a phosphate film is formed on the surface thereof. The invention relates to a method and an apparatus which are suitable for promptly forming a phosphate film having an excellent performance on such steel wires.

10 Background Art

[0002] In the cold drawing operation, the phosphate film is further covered by a lubricant such as metallic soap, and the phosphate film may carry the metallic soap forming a lubricating layer. In the cold drawing operation, the diameter of the steel wires becomes decreased by passing through several dies, and it is preferred that the phosphate film maintains its excellent performance until the steel wires pass through the last die.

15 [0003] The phosphate film is often formed by dipping the steel wires into a bath where a solution for making the phosphate film is contained, and no electrolytic devices are provided. In such a case, the productivity of the processing bath can be enhanced by increasing the travelling speed of the steel wires if a prompt formation of the phosphate film becomes possible.

20 [0004] Accordingly, a method is preferable which is able to form the phosphate film promptly. In order to promptly form the phosphate film, a liquid containing chemicals for forming a phosphate film with a high concentration has been used. However, in such a case, a great deal of sludge is produced in the liquid, and it must frequently be removed in order to obtain a phosphate film of excellent quality.

25 [0005] In the process of forming the phosphate film on the steel wires, the steel wires must be descaled previously by dipping them into a hydrochloric or sulfuric acid solution. Then, steel wires from which their oxide film has been removed by such a descaling process are dipped into the forming solution of phosphate film.

[0006] The inventors had found an electrolytic process where phosphate film can promptly be formed by using the steel wires as an electrolytic cathode in a solution which does not contain any complexing agent. Such a process is disclosed in JP-A-4-36498.

30 [0007] With the electrolytic process according to JP-A-4-36498, the productivity of phosphate film formation had been much enhanced. However, the process could not sufficiently improve the quality of the phosphate film and accordingly, the quality of the phosphate film obtained by that process was almost on the same level as that produced by a conventional process.

35 [0008] The document JP-A-6-322 592 discloses a process for forming a phosphate film on steel wires with an electrolytic process. However, in this conventional process, the steel wires are used as an anode. Also, the conventional process uses a pulsed electrolytic current in the electrolytic operation.

Disclosure of the Invention

40 [0009] As explained above, the productivity of phosphate film formation could be enhanced by the electrolytic process as disclosed in JP-A-4-36498, but the quality of the phosphate film could not be improved. The inventors have now made further investigations and studies and succeeded in finding a process and an apparatus for carrying out the method which are suitable to improve the quality of the phosphate film considerably.

45 [0010] According to new findings and understanding of the inventors, the quality of the phosphate film has a close relation with the descaling process of steel wires. As mentioned above, in the process of forming the phosphate film on the steel wires, the steel wires are descaled previously by dipping them into hydrochloric or sulfuric acid solution. In such a descaling process, an oxide film may be removed from the steel wires. However, the process leaves smut on the surface of the steel wires.

50 [0011] The smut formed may usually be removed by rinsing the steel wires in water. However, small amounts of smut remaining on the surface of the steel wires may form a phosphate film of insufficient quality. The smut may decrease the adhesive strength of the phosphate film on the surface of the steel wires, resulting in insufficient lubricating properties in a cold drawing operation of the steel wires and in insufficient surface properties of the final product of the steel wires.

55 [0012] Therefore, the purpose of the invention is to provide a new method and a new apparatus for carrying out the method which are suitable for promptly forming a phosphate film having a more excellent quality than those obtained by conventional processes on the steel wires of low carbon grades, high-carbon grades and low-alloy containing grades without generating any smut and any sludge.

[0013] According to a first aspect of the present invention, a method for forming a phosphate film on steel wires is

disclosed comprising a descaling process and a phosphate film forming process. The method is characterized in that the descaling process comprises an electrolytic pickling of steel wires using the steel wires as a cathode and using an acid solution other than phosphoric acid as an electrolyte, and in that the phosphate film forming process comprises an electrolytic process using the steel wires as a cathode and using a forming solution of phosphate film as an electrolyte.

[0014] According to a second aspect of the present invention, a method is disclosed for forming a phosphate film on steel wires comprising a descaling process, an intermediate process and a phosphate film process. The method is characterized in that the descaling process comprises an electrolytic pickling of the steel wires using the steel wires as a cathode and using acid other than phosphoric acid as an electrolyte, in that the intermediate process comprises a process of contacting the steel wires with an intermediate liquid containing colloidal titanium and alkali metal phosphate, and in that the phosphate film forming process comprises an electrolytic process using the steel wires as a cathode and using a forming solution of phosphate film as an electrolyte.

[0015] According to a third aspect of the present invention, a method is disclosed for forming a phosphate film on steel wires, wherein the steel wires for the descaling process are steel wires which are mechanically descaled as a pretreatment therefor.

[0016] According to a fourth aspect of the present invention, a method for forming a phosphate film on steel wires is disclosed wherein the electrolyte in the descaling process is selected from sulfuric acid, hydrochloric acid, nitric acid, hydrofluoric acid, hydrosilicofluoric acid and zircon hydrofluoric acid; a temperature of the electrolyte of 90 °C or lower is used in the descaling process; a current density of the steel wires of 1 A/dm<sup>2</sup> to 100 A/dm<sup>2</sup> DC is used and an electrolytic treatment time of 1 to 60 seconds is used in the descaling process.

[0017] According to a fifth aspect of the present invention, a method for forming a phosphate film on steel wires is disclosed wherein the electrolyte in the phosphate film forming process contains 2 to 60 g/l of zinc ions, 2 to 80 g/l of phosphoric acid ions and 3 to 100 g/l of nitric acid ions; a molar ratio of zinc ions to phosphoric acid ions is used which is 0.9 to 1.5, and a molar ratio of nitric acid ions to phosphoric acid ions is used which is 0.7 to 2.5; a temperature of the electrolyte of 90 °C or lower is used; a current density of the steel wires of 1 A/dm<sup>2</sup> to 100 A/dm<sup>2</sup> DC is used, and an electrolytic treatment time of 1 to 30 seconds is used in the phosphate film forming process.

[0018] According to a further aspect of the present invention, an apparatus for forming a phosphate film on the steel wires is disclosed comprising a descaling bath and a phosphate film forming bath. The apparatus is characterized in that the descaling bath comprises an electrolytic pickling bath of steel wires using steel wires as a cathode and using acid other than phosphoric acid as an electrolyte, and in that the phosphate film forming bath comprises an electrolytic film forming bath using the steel wires as a cathode and using a forming solution of phosphate film as an electrolyte.

[0019] According to a further aspect of the present invention, an apparatus for forming a phosphate film on steel wires is disclosed comprising a descaling bath, an intermediate bath and a phosphate film forming bath. The apparatus is characterized in that the descaling bath comprises an electrolytic pickling bath of steel wires using steel wires as a cathode and using acid other than phosphoric acid as an electrolyte; in that the intermediate bath comprises a bath of contacting the steel wires with an intermediate liquid containing colloidal titanium and alkali metal phosphate, and in that the phosphate film forming bath comprises an electrolytic film forming bath using steel wires as a cathode and using a forming solution of phosphate film as an electrolyte.

[0020] According to a still further aspect of the present invention, an apparatus for forming a phosphate film on steel wires is disclosed which is characterized in that the apparatus further comprises a mechanical descaler prior to the descaling bath.

[0021] According to yet another aspect of the present invention, an apparatus for forming a phosphate film on steel wires is disclosed which is characterized in that the apparatus further comprises an auxiliary acid pickling bath in-between the mechanical descaler and the descaling bath, and in that the auxiliary acid pickling bath is either one of a non electrolytic acid pickling bath or an electrolytic acid pickling bath using the steel wires as an anode.

#### Brief Description of the Drawing

[0022]

Fig. 1 is a diagrammatic view showing the main components of an apparatus according to the invention and suitable for carrying out the method according to the invention.

[0023] In Fig. 1, the following reference signs are used:

- 1 = Steel wires
- 2 = Descaling bath
- 3 = Phosphate film forming bath
- 4 = Auxiliary acid pickling bath

- 5 = Intermediate bath
- 6 = Mechanical descaler
- 7 = Uncoiler
- 8 = Coiler

5

### Best Modes for Carrying out the Invention

[0024] The inventors have investigated surfaces of steel wires after a pickling treatment. When a conventional acid pickling is used, such as dipping steel wires into hydrochloric acid or sulfuric acid, many large pitting holes can be observed on the surface of the steel wires; also, many dark coloured smuts can be observed which are generated or composed by deposit and redeposit of insoluble and soluble compounds such as carbon, ferric oxides or the like adhering on the surface of steel wires. On the other hand, when using the electrolytic pickling process according to the present invention, no such smut was observed and the surfaces of the steel wires were very clean.

[0025] When the steel wires are used as a cathode, a cathode reaction of generating a hydrogen gas may occur in a short time on the surface of the steel wires and the physical movement of the hydrogen gas may clean the surface of the steel wires. Also, hydrogen ions gathering in a high concentration near the surface of the steel wires may clean the surface of steel wires. Thereby, the surface of steel wires is less roughened and no smut is formed thereon.

[0026] According to the invention, the electrolysis is carried out by using the steel wires as a cathode. On the other hand, in a conventional process, the electrolysis is carried out by using the steel wires as an anode. In such an anode electrolysis, the iron may dissolve into the electrolytic solution as iron ions, and the iron ions may be a cause of the smut on the surface of steel wires.

[0027] In the usual descaling of steel wires by dipping them into the acids, the iron may also dissolve into the acid solution as iron ions, and the iron ions may become the cause of smut on the surface of steel wires.

[0028] According to the invention, however, the electrolysis is carried out by using the steel wires as a cathode and  $H^+$  ions are attracted toward the steel wires and are discharged on the surface of the steel wires so that  $H_2$  gas is generated from the steel wires. Thus the cathode electrolysis of the invention is not an electrolysis dissolving the iron as iron ions, and no smut is generated on the surface of the steel wires.

[0029] Further investigations made by the inventors have revealed that in the conventional method, where the anode pickling is carried out before the phosphate film forming process, much slugs can be observed in the phosphate film forming bath.

[0030] Also, the performance of the phosphate film as a lubricating layer becomes decreased in such a case.

[0031] According to the present invention, the descaling is carried out by using the steel wires as a cathode. Experiments of the inventors have revealed that the steel wires - when the cathode electrolytic pickling is carried out - never generate any sludge in the subsequent process of forming the phosphate film. Also, when using this cathode electrolytic pickling, no smut is generated on the surface of the steel wires, and the adhesive strength of the phosphate film to the surface of the steel wires is considerably enhanced and the performance of producing a lubricating layer is remarkably improved.

[0032] A sulfuric acid solution is preferably used for the electrolytic pickling in the method according to the invention, and either one or more than one selected from sulfuric acid, hydrochloric acid, nitric acid, hydrofluoric acid, hydrosilicofluoric acid and zircon hydrofluoric acid may be used. The acid concentration is preferably in the range of 5 to 40 %.

[0033] In the electrolytic pickling according to the invention, preferably a current density of 1 to 100 A/dm<sup>2</sup>, and more preferably of 20 to 50 A/dm<sup>2</sup> direct current is used. When the current density is less than 1 A/dm<sup>2</sup>, the generated amount of hydrogen gas is small and a sufficient washing strength is not obtainable. Also, a current density higher than 100 A/dm<sup>2</sup> is economically not preferable because an early degradation of the processing liquid may result. The liquid temperature is 90 °C or less, preferably in the range of 50 to 80 °C. The processing time is preferably 1 to 60 seconds, more preferably 1 to 30 seconds.

[0034] In the case of hot rolled steel wires and heat treated steel wires, the surfaces of steel wires are often covered by thick scale. In order to remove this thick scale from the surfaces of steel wires, usually a mechanical descaling is carried out thereon, such as bending descaling, shot blast descaling, air blast descaling or the like. The descaling by cathode electrolytic pickling is carried out after the mechanical descaling.

[0035] However, when such a mechanical descaling is insufficient, another conventional acid pickling of using a non-electrolytic pickling bath or using an electrolytic acid pickling bath may be applied after the mechanical descaling wherein the steel wires are used as an anode. In such a case, however, the cathode electrolytic pickling according to the invention has to be carried out after the conventional acid pickling as mentioned above.

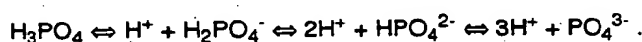
[0036] In the method according to the invention, the phosphate film forming process is carried out after the descaling process of cathode electrolytic pickling. It is known that the structure of the phosphate film becomes fine and improved when the steel wires are contacted with a liquid wherein colloidal titanium and alkali metal phosphate are contained. When this process is applied in the method according to the invention, an intermediate bath, wherein a liquid compris-

ing colloidal titanium and alkali metal phosphate is contained, may be provided between the descaling bath and the phosphate film forming bath; hence, the steel wires are brought into contact with the intermediate liquid after the cathode electrolytic pickling.

[0037] As explained above, sufficiently clean surfaces of steel wires are difficult to obtain by a conventional descaling process. However, in the method according to the present invention, cathode electrolytic pickling is carried out after a conventional descaling process, and sufficiently clean surfaces of steel wires are obtained by such a cathode electrolytic pickling.

[0038] In the method according to the invention, after the cathode electrolytic pickling, the phosphate film forming process is carried out by using the direct current electrolysis, using the steel wires as a cathode and using a phosphate film forming liquid as an electrolyte.

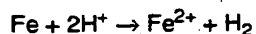
[0039] The phosphoric acid in the phosphate film forming liquid may dissociate according to the following equation:



[0040] In the above equation,  $\text{PO}_4^{3-}$  ions may combine with metallic ions and may produce a metal phosphate compound. Such a metal phosphate compound is deposited on the surfaces of steel wires and may become a suitable phosphate film. When  $\text{H}^+$  ions in the phosphate film forming liquid are present in a high concentration near the steel wires, the above equation may proceed to the left direction; hence, the  $\text{PO}_4^{3-}$  content near the steel wires may decrease, and the phosphate compound is not formed.

[0041] On the other hand, when the  $\text{H}^+$  ion concentration in the phosphate film forming liquid becomes low, the above equation may proceed to the right direction; hence, the  $\text{PO}_4^{3-}$  content near the steel wires may increase, and the metal phosphate compound is formed and deposited on the surfaces of the steel wires.

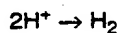
[0042] In the conventional dipping process, the steel wires are corroded by the phosphate film forming liquid in accordance with the chemical reaction of



In this chemical reaction,  $\text{H}^+$  ions near the steel wires may be consumed and their concentration may decrease, while the  $\text{PO}_4^{3-}$  ion concentration near the steel wires may increase, and the metal phosphate compound is produced on the surfaces of the steel wires.

[0043] However, in the conventional process as indicated above, Fe has to be changed into  $\text{Fe}^{2+}$ , and the  $\text{Fe}^{2+}$  ions have to be dissolved into the phosphate film forming liquid, wherein the dissolved  $\text{Fe}^{2+}$  ions may cause the trouble of producing smut and sludge.

[0044] On the other hand, in the method according to the present invention, the direct current electrolysis is carried out by using the steel wires as a cathode. In this cathode electrolysis,  $\text{H}^+$  ions are attracted to the cathode and are consumed in the discharge reaction of



[0045] As the result of this discharge reaction, the  $\text{H}^+$  ion concentration near the steel wires becomes low, and the  $\text{PO}_4^{3-}$  ion concentration becomes high so that the metal phosphate compound is deposited on the surfaces of the steel wires.

[0046] Namely, according to the present invention, the  $\text{H}^+$  ion concentration near the steel wires is decreased by the electrolytical discharge. Accordingly, the iron does not dissolve into the phosphate film forming liquid, and smut and sludge which are otherwise produced by dissolved iron ions do not appear in the method according to the present invention.

[0047] In the conventional dipping process of forming the phosphate film, Fe is dissolved and the  $\text{H}^+$  ion concentration is lowered, wherein the phosphate film is formed with the velocity according to the lowering speed of the  $\text{H}^+$  ion concentration. However, it is hard to dissolve Fe with a high speed and accordingly it is difficult to form a phosphate film with high speed.

[0048] On the other hand, in the method according to the present invention, the  $\text{H}^+$  ion concentration is decreased by the discharge of  $\text{H}^+$  ions, and the velocity of discharge of  $\text{H}^+$  ions may be controlled by adjusting the current density of the electrolytic process. Hence, in the method according to the present invention, it is possible to form the phosphate film with high speed by controlling the current density of the electrolytic process.

[0049] Also, the following aspect was revealed by the inventors. Even if the method of forming the phosphate film is a cathode electrolysis as in the invention, the performance of the phosphate film is insufficient when the pickling is not carried out by the process of cathode electrolysis. When the descaling is made by the cathode electrolysis of the inven-

tion and the phosphate film production is carried out by the cathode electrolysis of the invention, the resulting phosphate film having a sufficient performance is formed with high speed.

[0050] As to the electric terminals for connecting the steel wires to an electric power supply source, bipolar type electric terminals can be used in the present invention. With such bipolar type electric terminals, the electrodes of the electric supply source are immersed in the electrolyte, and the electric current is supplied to the steel wires via the electrolyte. In the case of using bipolar type electric terminals, the electrodes of the electric power supply source do not contact with the steel wires directly, and the phosphate film may be produced smoothly without creating any defects on the surface of the steel wires and the phosphate film.

[0051] The forming solution of phosphate film in the method according to the invention may preferably contain zinc ions in an amount of 2 to 60 g/l, phosphoric acid ions in an amount of 2 to 80 g/l and nitric acid ions in an amount of 3 to 100 g/l; moreover, the forming solution is a liquid wherein the molar ratio of the zinc ions to the phosphoric acid ions is 0.9 to 1.5 and wherein the molar ratio of nitric acid ions to the phosphoric acid ions is 0.7 to 2.5.

[0052] When the concentration of zinc ions, phosphoric acid ions and nitric acid ions is lower than the above-indicated ranges, the phosphate film cannot easily be formed. Also, exceeding the above values or ranges is not preferable under economical aspects and the adhesive property of the phosphate film to the steel wires is decreased thereby.

[0053] When the molar ratio of (zinc ions/phosphoric acid ions) is less than 0.9, a zinc eutectoid occurs, and a good film is difficult to obtain and the adhesive property of the phosphate film becomes worse. However, exceeding the value of 1.5 is not preferred economically. Also, when the molar ratio of (nitric acid ions/phosphoric acid ions) is less than 0.7, the stability of the liquid is decreased, whereas when exceeding the value of 2.5, the required film weight is hard to obtain due to a self oxidation.

[0054] Furthermore, nickel phosphate, manganese phosphate, calcium phosphate may be contained in the forming solution of phosphate film. Moreover, nitrous acid ions, hydrogen peroxide and chloric acid ions can be added as an oxidant.

[0055] When the oxidant comprises nitrous acid ions, the content thereof is preferred to be 0.05 to 0.18 g/l. The inventors picked up the electrolyte by 10 ml and using phenolphthalein as an indicator, titrated this with 0.1 N-NaOH solution and called the ml of 0.1 N-NaOH solution as a point, wherein the electrolyte is preferred to be in the range of 5 to 200 points.

[0056] The electrolysis of the phosphate film formation is preferably carried out by using a temperature of the electrolyte of 90 °C or less, more preferably in the range of 50 to 80 °C. Also, the current density of the direct current is probably in the range of 1 to 100 A/dm<sup>2</sup>, more preferably in the range of 20 to 50 A/dm<sup>2</sup>. When the current density is less than 1 A/dm<sup>2</sup>, then the phosphate film is not easily formed, and when it exceeds 100 A/dm<sup>2</sup>, the adhesive properties of the film may be decreased.

[0057] In a conventional process it is known that the steel wires may be contacted with a liquid containing a colloidal titanium and alkali metal phosphate salt, and thereafter the phosphate film is formed. In such a process, the titanium compound absorbed on the steel wires becomes a core of a crystal of the deposited phosphate, and thereby a phosphate film having a fine structure may be obtained.

[0058] In the method according to the present invention, the contact of the steel wires with a liquid containing colloidal titanium and alkali metal phosphate salt may be carried out after the descaling process and before the phosphate film forming process. Hence, the phosphate film is further improved by such a treatment. Namely, an extremely preferable lubricating phosphate film having excellent adhesive properties and an excellent fineness is obtained.

[0059] In this treatment, the same liquids as those used in the conventional process may be used. Such liquids may contain colloidal titanium, pyrophosphoric acid ions, orthophosphoric acid ions and sodium ions, as described for example in JP-A-3-38 343 and JP-A-6-74 507. The steel wires may be dipped into such treatment liquids at room temperature for about 1 to 5 seconds.

[0060] In the cathode electrolysis of the phosphate film formation according to the present invention, the pH value of the electrolyte is preferred to be set near the pH range suitable for depositing of Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>. In order to keep the pH value of the electrolyte near this pH range, the equilibrium constant *k* mentioned below is able to create a suitable standard.

$$k = \{ [\text{Zn}_3(\text{PO}_4)_2] \times [\text{H}_3\text{PO}_4]^4 \} / \{ \text{Zn}(\text{H}_2\text{PO}_4)_2 \}^3$$

[0061] Also, more simply, the acid ratio given below can be used:

$$\{ \text{total acidity (point)} \} / \{ \text{free acidity (point)} \}$$

[0062] The relation between the temperature and the acid ratio is preferred to keep the acid ratio in the range of 4.5 to 6 at temperatures higher than 80 °C, and in the range of 6 to 9 at temperatures of 60 to 80 °C. When the treatment temperature is low, the higher acid ratio may be preferable in order to form the phosphate film easily.

[0063] In the phosphate film forming process by the cathode electrolysis, the phosphate film can be formed more efficiently by controlling the quantity of the effective components. As a standard of this control of the amount of the effective components, it is preferable to keep the value of the following equation in the range of 2.5 to 6.0:

$$\{(\text{total acidity (TA)} - \text{free acidity (FA)}) / \{\text{free acidity (FA)}\}\}.$$

[0064] By such a control, it is possible to promptly obtain a high quality phosphate film. In the case of steel wires, a hard steel wire is most preferable, wherein

$$\{(\text{TA}) - (\text{FA})\} / \{(\text{FA})\} = 3.5 \text{ to } 5.5.$$

[0065] Fig. 1 discloses a diagrammatic example of the apparatus according to the invention. The apparatus comprises a descaling bath 2 for electrolytic descaling steel wires 1 using the steel wires 1 as a cathode. Further to the descaling bath 2, a phosphate film forming bath 3 is provided for forming the phosphate film on the steel wires 1 by electrolysis using the steel wires 1 as a cathode.

[0066] In the descaling bath 2, the electrolyte is contained which is selected from acids other than phosphoric acid, for example sulfuric acid, hydrochloric acid, nitric acid, hydrofluoric acid, hydrosilicofluoric acid, zircon hydrofluoric acid or the like. Then, the steel wires 1 are cleaned by the cathode electrolytic pickling, for example by using direct current with a current density in the range of 1 A/dm<sup>2</sup> to 100 A/dm<sup>2</sup>.

[0067] In the phosphate film forming bath 3, the phosphate film forming liquid is contained and comprises, for example, zinc ions, phosphoric acid ions and nitric acid ions. The phosphate film is formed on the steel wires 1 using a current density in the range of, for example, 1 A/dm<sup>2</sup> to 100 A/dm<sup>2</sup>.

[0068] Also, Fig. 1 shows a contact roller for an electric terminal for contacting the steel wires 1 with the electric power supply source; however, other non-contact electric terminals, for example bipolar type electric terminals can be used. As an anode in the apparatus according to Fig. 1, an insoluble anode is used, for example Pt coated on a titanium or graphite electrode can be used.

[0069] In the apparatus according to the invention, an intermediate bath 5 may also be provided after the descaling bath 2 and before the phosphate film forming bath 3. This intermediate bath 5 contains a surface adjusting liquid including colloidal titanium and alkali metal salt.

[0070] When the steel wires 1 are brought into contact with such a surface adjusting liquid, a fine phosphate film of excellent quality is formed in the phosphate film forming bath 3.

[0071] In the apparatus of Fig. 1, a mechanical descaler 6 is provided which is of the type comprising three rollers. However, as a mechanical descaler, a different type of mechanical type of descaler may be used such as a shot blast descaler or the like.

[0072] The reference sign 4 in Fig. 1 is an example of an auxiliary acid pickling bath which is arranged before the descaling bath 2. This auxiliary pickling bath 4 may be an acid pickling bath using the steel wires 1 as an anode or a non-electrolytic acid pickling bath which is used in order to mitigate the workload of the descaling bath 2.

[0073] Although not shown in Fig. 1, a generally known water rinsing apparatus or a hot water rinsing apparatus may be provided between the respective baths in order to prevent that a liquid of a preceding bath is brought into the following bath. Also, a generally known stirring apparatus for liquids can be arranged with the respective bath in order to enhance the reactivity of the steel wires 1 with the liquids contained in each of the baths.

[0074] Moreover, a counter-flow installation can be used in each of the baths to obtain a flow of the liquid against the running direction of the steel wires 1 in order to promote the reaction in the respective bath. In the apparatus according to Fig. 1, an uncoiler 7 for the untreated steel wires 1 and a coiler 8 for the treated steel wires 1 are provided.

#### Embodiment Example and Comparative Example

[0075] JIS-SWRH72A steel wires with a C content of 0.72 wt.-% having a diameter of 5.5 mm are cold drawn by a continuous drawing method.

[0076] Before the cold drawing operation, phosphate films are formed on the surfaces of the steel wires with different methods. Table 1 shows an outline thereof. All steel wires were mechanically descaled previously, and a scale of 90 % or more was removed. A usual metallic soap powder obtained in the market is used as a lubricant in cold drawing.

[0077] In the descaling column of Table 1, process C indicates an electrolytic pickling using the steel wires as a cathode, and the process A indicates an electrolytic pickling using the steel wires as an anode. In this descaling column, the process of A → C indicates an example wherein the anodic electrolysis is carried out in the first half of the pickling time, and the second half of the pickling time is carried out in a cathode electrolysis.

[0078] On the other hand, the process of C → A indicates that the first half is a cathodic process and the second half is an anodic process. In this column, the process of "dip" indicates a non-electrolytic process. All the electrolytes as well



as the dipping solutions are sulfuric acid having a concentration of 25 %.

[0079] In the intermediate column of Table 1, symbol ○ shows the contacting with the intermediate solution comprising colloidal titanium and alkali metal phosphate produced by using PREPAREN 2 which is a product available from Nihon Parkerizing Co. Ltd.

[0080] In the phosphate film forming column in Table 1, the process C indicates an electrolysis using the steel wires as a cathode, and the process "dip" indicates non-electrolysis. An electrolyte as well as a dipping solution are produced by using PARBOND-TD-805, a commercially available phosphate film forming agent produced by Nihon Parkerizing Co., Ltd., and the total acid of the liquid is adjusted to be 90 points.

[0081] In the phosphate film forming column of Table 1, the column "Before (g/m<sup>2</sup>)" indicates an amount of the phosphate film measured before cold drawing, and the column "After (g/m<sup>2</sup>)" indicates an amount of the phosphate film measured after cold drawing. The amount of phosphate film can be determined by dipping the steel wires into an aqueous solution containing chromic acid by 5 %, thereby removing all the phosphate film from the steel wires. Then, the amount of the phosphate film may be determined by measuring the weight of the steel wires before and after the chromic acid treatment.

[0082] In the same column of Table 1, "Crystal Size" indicates the crystal sizes in μm of the phosphate film measured by using a scanning electron microscope.

[0083] The column "Sludge" in Table 1 shows the amount of sludge in the phosphate film forming solution measured after using it in operation for one hour. The indication ○ is representative for a transparent solution without sludge, the reference sign Δ is representative for little sludge of less than 3 g/l, and the reference sign X is representative for much sludge of more than 3 g/l.

[0084] The column "Drawability" in Table 1 comprises the symbol ⊙ in a case wherein more than 50 tons of steel wires were cold drawn through the final die; the symbol ○ indicates a case wherein 15 to 50 tons of steel wires could be cold drawn through the final die; and the symbol Δ represents a case wherein less than 15 tons of steel wires could be cold drawn through the final die; the symbol X indicates a case wherein a defective product was produced in cold drawing.

[0085] The Embodiment Examples Nos. 1 to 12 in Table 1 show that the descaling process and the phosphate film forming process were performed by electrolytic processes, and the electric processes were carried out according to the teaching of the present invention. In these Examples, no sludge was observed in the phosphate film forming solution and the drawability of the products was excellent. In the Embodiments Nos. 1 to 9 in Table 1, the products were treated in the intermediate bath, and the crystal size of the phosphate film was finer than those of the Embodiments Nos. 10 to 12 wherein the treatment in the intermediate bath was not carried out.

[0086] Corresponding data in the respective columns were obtained for Comparative Examples No. 1 to No. 8. In these Comparative Examples, the current density A/dm<sup>2</sup> in the descaling process is too low in Comparative Example No. 1; the current density A/dm<sup>2</sup> of the phosphate film forming process is too high in Comparative Example No. 2; the descaling process was non-electrolytic in Comparative Examples Nos. 3 and 4; the phosphate film forming process was non-electrolytic in Comparative Examples Nos. 3 and 5; and the treating time in seconds in the phosphate film forming process is too short in Comparative Example No. 6. Also, in these Comparative Examples, the sludge decreasing effect and the drawability were insufficient.

[0087] In the Embodiment Examples Nos. 13 and 14, the first half of the descaling process was anodic electrolysis, however, the second half was a cathodic electrolysis. In these cases, the sludge decreasing effect and the drawability were excellent. On the other hand, in the Comparative Examples Nos. 7 and 8, the first half of the descaling process was a cathodic electrolysis and the second half was an anodic electrolysis. In these cases, the sludge decreasing effect and the drawability were insufficient.

[0088] In the Comparative Example No. 3, the phosphate film forming process was carried out by dipping for 5 seconds, and the amount of produced phosphate film was 6.2 g/m<sup>2</sup>. However, this value of 6.2 g/m<sup>2</sup> is less than the amount of phosphate film obtained in Embodiment Examples of Nos. 1 to 14 wherein the phosphate film forming was carried out by cathodic electrolysis. In the same way, as shown in Comparative Example No. 5, the amount of phosphate film of 3.5 g/m<sup>2</sup> obtained by a dipping process is less than that obtained in the Embodiment Examples Nos. 1 to 14.

[0089] The examples compiled in Table 1 are examples performed on steel wires of high carbon grade. Even though not shown specifically in the present specification, similar tests were also carried out on steel wires of low carbon grades and low alloy containing grades. Similar results as those shown in Table 1 were obtained in the latter cases when using the method and the apparatus according to the invention.

#### Advantages of the Invention

[0090] According to the invention, it is possible that a phosphate film of more excellent performance for cold drawing can promptly be formed on steel wires of low carbon grade, high carbon grade and low alloy containing grade when compared with conventional methods. Also, activities for removing sludges from the liquid baths can be decreased



because no such sludges are produced in the method according to the invention.

Table 1

	Descaling				Inter- medi- ate	Phosphate Film Forming						Sludge	Draw ability		
	Process	A/dm <sup>2</sup>	°C	sec.		Process	A/dm <sup>2</sup>	°C	sec.	Before (g/m <sup>2</sup> )	After (g/m <sup>2</sup> )			Crystal Size (μm)	
embodiment example	1	C	1	90	20	O	C	100	70	1	8.1	1.6	2~5	O	O
	2	C	10	90	10	O	C	100	70	1	8.4	1.7	2~5	O	O
	3	C	20	80	5	O	C	70	80	2	9.8	1.8	2~5	O	⊙
	4	C	30	80	5	O	C	50	80	5	11.4	2.0	2~5	O	⊙
	5	C	30	80	5	O	C	25	80	5	9.8	1.9	2~5	O	⊙
	6	C	50	80	5	O	C	30	80	5	10.0	1.9	2~5	O	⊙
	7	C	70	70	2	O	C	20	80	10	11.1	1.9	2~5	O	O
	8	C	90	70	1	O	C	10	90	10	10.2	1.8	2~5	O	O
	9	C	100	50	1	O	C	1	90	20	8.0	1.7	2~5	O	O
	10	C	5	80	10	—	C	10	80	5	8.5	1.1	20~30	O	O
	11	C	25	70	20	—	C	50	50	15	9.2	1.3	20~30	O	O
	12	C	50	50	5	—	C	100	70	10	10.9	1.3	20~30	O	O
	13	A→C	30	80	5	O	C	25	80	5	11.8	1.1	2~5	O	⊙
	14	A→C	30	80	5	—	C	25	80	5	10.1	1.0	20~30	O	O
comparative example	1	C	0.5	90	1	O	C	0.5	90	20	5.4	0.1	5~10	Δ	×
	2	C	20	90	5	O	C	150	80	10	15.0	0	2~5	Δ	×
	3	Dip	0	70	5	O	Dip	0	70	5	6.2	0.4	10~20	×	Δ
	4	Dip	0	80	10	O	C	10	70	10	9.6	0.7	10~20	Δ	Δ
	5	C	25	60	10	—	Dip	0	80	2	3.5	0	20~30	×	×
	6	C	25	80	10	O	C	20	80	0.5	1.5	0	5~10	O	×
	7	C→A	30	80	5	O	C	25	80	5	9.6	1.1	5~10	Δ	Δ
	8	C→A	30	80	5	—	C	25	80	5	9.3	0.9	20~30	Δ	×

## Claims

- 55 1. A method for forming a phosphate film on steel wires comprising a descaling process (2) and a phosphate film forming process (4),  
characterized in that the descaling process (2) comprises an electrolytic pickling of steel wires using the steel wires as a cathode and using acid other than phosphoric acid as an electrolyte,

and in that the phosphate film forming process (4) comprises an electrolytic process using the steel wires as a cathode and using a forming solution of phosphate film as an electrolyte.

2. A method for forming a phosphate film on steel wires comprising a descaling process (2), an intermediate process (5) and a phosphate film forming process (3),  
characterized in that the descaling process (2) comprises an electrolytic pickling of the steel wires using the steel wires as a cathode and using acid other than a phosphoric acid as an electrolyte,

in that the intermediate process (5) comprises a process of contacting the steel wires with an intermediate liquid containing colloidal titanium and alkali metal phosphate, and in that the phosphate film forming process (3) comprises an electrolytic process using the steel wires as a cathode and using a forming solution of phosphate film as an electrolyte.

3. The method according to claim 1 or 2,  
characterized in that the steel wires for the descaling process (2) are steel wires which are mechanically descaled (6) as a pretreatment therefor.

4. The method according to any of claims 1 to 3,  
characterized in that the electrolyte in the descaling process (2) is selected from sulfuric acid, hydrochloric acid, nitric acid, hydrofluoric acid, hydrosilicofluoric acid and zircon hydrofluoric acid,

in that a temperature of the electrolyte of 90 °C or lower is used in the descaling process (2),  
in that a current density of the steel wires of 1 A/dm<sup>2</sup> to 100 A/dm<sup>2</sup> D.C. is used,  
and in that an electrolytic treatment time of 1 to 60 seconds is used in the descaling process (2).

5. The method according to any of claims 1 to 4,  
characterized in that the electrolyte in the phosphate film forming process (4) contains 2 to 60 g/l of zinc ions, 2 to 80 g/l of phosphoric acid ions and 3 to 100 g/l of nitric acid ions,

in that the molar ratio of zinc ions to phosphoric acid ions is 0.9 to 1.5 and the molar ratio of nitric acid ions to phosphoric acid ions is 0.7 to 2.5,  
in that a temperature of the electrolyte of 90 °C or lower is used,  
in that a current density of the steel wires of 1 A/dm<sup>2</sup> to 100 A/dm<sup>2</sup> D.C. is used,  
and in that an electrolytic treatment time of 1 to 30 seconds is used in the phosphate film forming process (3).

6. An apparatus for forming a phosphate film on steel wires comprising a descaling bath (2) and a phosphate film forming bath (3),  
characterized in that the descaling bath (2) comprises an electrolytic pickling bath of steel wires using steel wires as a cathode and using acid other than phosphoric acid as an electrolyte,

and in that the phosphate film forming bath (3) comprises an electrolytic film forming bath using the steel wires as a cathode and using a forming solution of phosphate film as an electrolyte.

7. An apparatus for forming phosphate film on steel wires comprising a descaling bath (2), an intermediate bath (5) and a phosphate film forming bath (3),  
characterized in that the descaling bath (2) comprises an electrolytic pickling bath of steel wires using steel wires as a cathode and using acid other than phosphoric acid as an electrolyte,

in that the intermediate bath (5) comprises a bath of contacting the steel wires with an intermediate liquid containing colloidal titanium and alkali metal phosphate,  
and in that the phosphate film forming bath (3) comprises an electrolytic film forming bath using steel wires as a cathode and using a forming solution of phosphate film as an electrolyte.

8. The apparatus according to claim 6 or 7,  
characterized in that the apparatus further comprises a mechanical descaler (6) prior to the descaling bath (2).

9. The apparatus according to claim 8,  
characterized in that the apparatus further comprises an auxiliary acid pickling bath (4) in-between the mechanical

descaler (6) and the descaling bath (2).

and in that the auxiliary acid pickling bath (4) is either one of non electrolytic acid pickling bath or an electrolytic acid pickling bath using the steel wires as an anode.

5

10

15

20

25

30

35

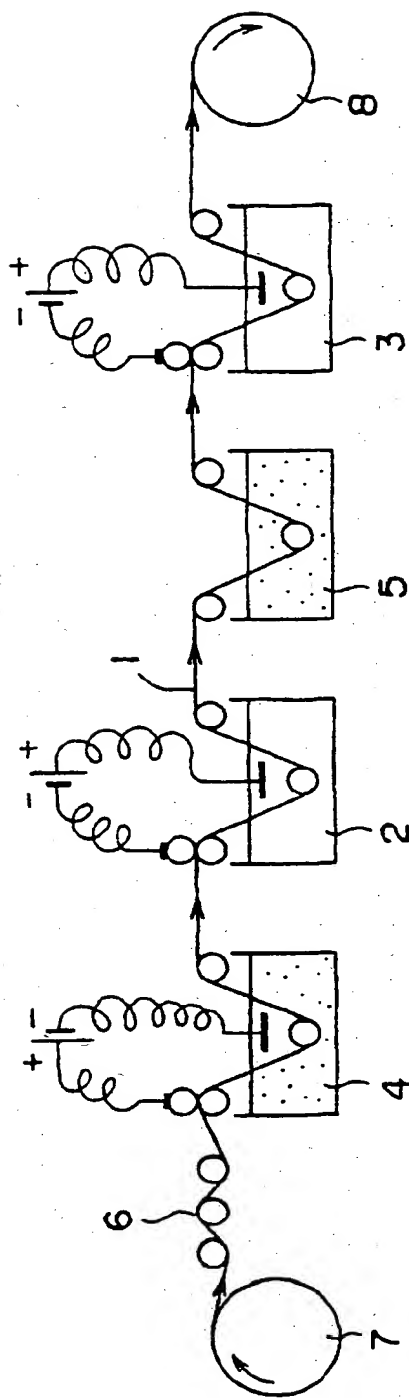
40

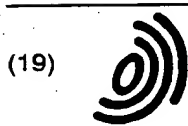
45

50

55

Fig. 1





Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11)

**EP 0 972 862 A3**

(12)

# EUROPEAN PATENT APPLICATION

(88) Date of publication A3:  
02.01.2004 Bulletin 2004/01

(51) Int Cl.7: C25D 11/36, C25F 1/00

(43) Date of publication A2:  
19.01.2000 Bulletin 2000/03

(21) Application number: 99112414.0

(22) Date of filing: 29.06.1999

(84) Designated Contracting States:  
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE  
Designated Extension States:  
AL LT LV MK RO SI

(30) Priority: 01.07.1998 JP 18583098

(71) Applicants:  
• NIHON PARKERIZING CO., LTD.  
Chuo-ku, Tokyo (JP)  
• Fujisyouji K.K.  
Hashimashi, Gifu 501-6257 (JP)

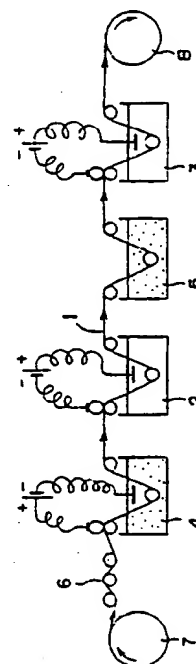
(72) Inventors:  
• Kobayashi, Naoyuki,  
c/o Nihon Parkerizing Co., Ltd  
Tokyo (JP)  
• Moriyama, Atsushi,  
c/o Nihon Parkerizing Co., Ltd  
Tokyo (JP)  
• Takagi, Shigemasa, c/o Fujisyouji K.K.  
Gifu 501-6257 (JP)  
• Katsumata, Tomoaki, c/o Fujisyouji K.K.  
Gifu 501-6257 (JP)

(74) Representative: Sajda, Wolf E., Dipl.-Phys. et al  
MEISSNER, BOLTE & PARTNER  
Widenmayerstrasse 48  
80538 München (DE)

(54) **Method for forming a phosphate film on steel wires and apparatus used therefor**

(57) A method and an apparatus are disclosed which are suitable for promptly forming a phosphate film of excellent performance for cold drawing on steel wires (1). The steel wires (1) are descaled by a cathodic electrolysis in an acid solution, and thereafter, a phosphate film is formed by a cathodic electrolysis on the steel wires. Contacting with a solution containing colloidal titanium is preferably carried out between a cathodic descaling process (2) and a phosphate film forming process (3). Descaling in a cathodic electrolysis may be performed in an acid solution at a temperature of lower than 90 °C and with a current density of 1 to 100 A/dm<sup>2</sup>. Phosphate film forming (3) may be performed by using an electrolyte containing Zn ions, phosphoric acid ions and nitric acid ions, at a temperature of lower than 90 °C with a current density of 1 to 100 A/dm<sup>2</sup> and for a period of 1 to 30 seconds.

Fig.1



EP 0 972 862 A3



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 99 11 2414

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A, D	WO 91 19836 A (HENKEL CORP) 26 December 1991 (1991-12-26) ---		C25D11/36 C25F1/00
A, D	EP 0 201 841 A (NIHON PARKERIZING) 20 November 1986 (1986-11-20) ---		
A	US 4 188 812 A (FURUYA TAKASHI ET AL) 19 February 1980 (1980-02-19) ---		
A	US 4 437 947 A (HIROSE KIKUJI ET AL) 20 March 1984 (1984-03-20) ---		
A	US 4 808 278 A (ROBBINS DOUGLAS J ET AL) 28 February 1989 (1989-02-28) ---		
A	GB 1 165 014 A (KENMORE) 24 September 1969 (1969-09-24) -----		
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.7)  C25D C25F
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>4 November 2003</b>	Examiner <b>Van Leeuwen, R</b>
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03 02 (04/2001)

ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.

EP 99 11 2414

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

04-11-2003

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9119836 A	26-12-1991	JP 4036498 A WO 9119836 A1	06-02-1992 26-12-1991
EP 0201841 A	20-11-1986	JP 1675251 C JP 3038343 B JP 61257481 A AT 68532 T AU 5672986 A BR 8602096 A DE 3615294 A1 DE 3681958 D1 EP 0201841 A2 GB 2174719 A , B	26-06-1992 10-06-1991 14-11-1986 15-11-1991 13-11-1986 13-01-1987 13-11-1986 21-11-1991 20-11-1986 12-11-1986
US 4188812 A	19-02-1980	NONE	
US 4437947 A	20-03-1984	JP 1222521 C JP 56116887 A JP 58037391 B BR 8101053 A CA 1162444 A1 DE 3172940 D1 EP 0035193 A1	15-08-1984 12-09-1981 16-08-1983 25-08-1981 21-02-1984 02-01-1986 09-09-1981
US 4808278 A	28-02-1989	AT 74631 T AU 2671088 A BR 8900131 A CA 1337554 C DE 3869938 D1 EP 0324116 A2 ES 2031989 T3 JP 1219200 A US 4814054 A	15-04-1992 20-07-1989 05-09-1989 14-11-1995 14-05-1992 19-07-1989 01-01-1993 01-09-1989 21-03-1989
GB 1165014 A	24-09-1969	CH 472513 A US 3399702 A BE 689972 A DE 1796363 A1 DE 1621610 A1 GB 1165015 A US 3501347 A	15-05-1969 03-09-1968 02-05-1967 09-09-1976 27-05-1971 24-09-1969 17-03-1970

EPO FORM P0452

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82



**THIS PAGE BLANK (USPTO)**